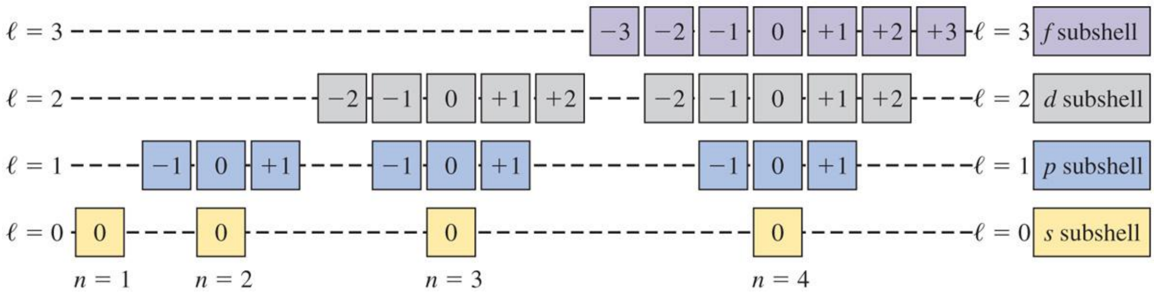
Quantum Mechanics

- **Heisenberg's equation disproved Bohr's model of defined orbits for electrons**
- **Bohr's theory did not provide a clear description**
- **Erwin Schrödinger, derived a complex mathematical formula to incorporate wave and particle characteristics**

Quantum Numbers

- **Each atomic orbital in an atom is characterized by a unique set of three quantum numbers (from Schrödinger's wave equation)**
- **n, l, and m_l**
- ***Magnetic quantum number* (m_l) - describes the orientation of the orbital in space (think in terms of x, y and z axes)**
- **Integer values: $-l$ to 0 to $+l$**



Which of the following are possible sets of quantum numbers?

a) 1, 1, 0, +1/2

b) 2, 0, 0, +1/2

c) 3, 2, –2, –1/2

- ***Electron spin quantum number* (m_s) - describes the spin of an electron that occupies a particular orbital**
- **Values: +1/2 or –1/2**
- **Electrons will spin opposite each other in the same orbital**

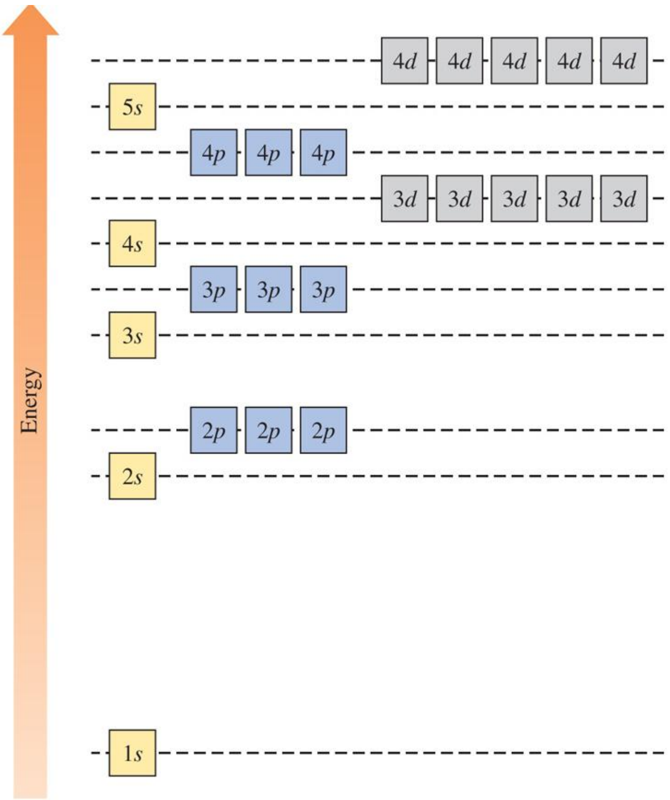
Atomic Orbitals

- **"Shapes" of atomic orbitals**
- **"*s*" orbital - spherical in shape**
- **"*p*" orbitals - two lobes on opposite sides of the nucleus**
- **"*d*" orbitals - more variations of lobes**
- **"*f*" orbitals - complex shapes**

Electron Configuration

- *Ground state* - electrons in lowest energy state
- *Excited state* - electrons in a higher energy orbital
- *Electron configuration* - how electrons are distributed in the various atomic orbitals

Electron Configuration - Notice the Energy for Each Orbital



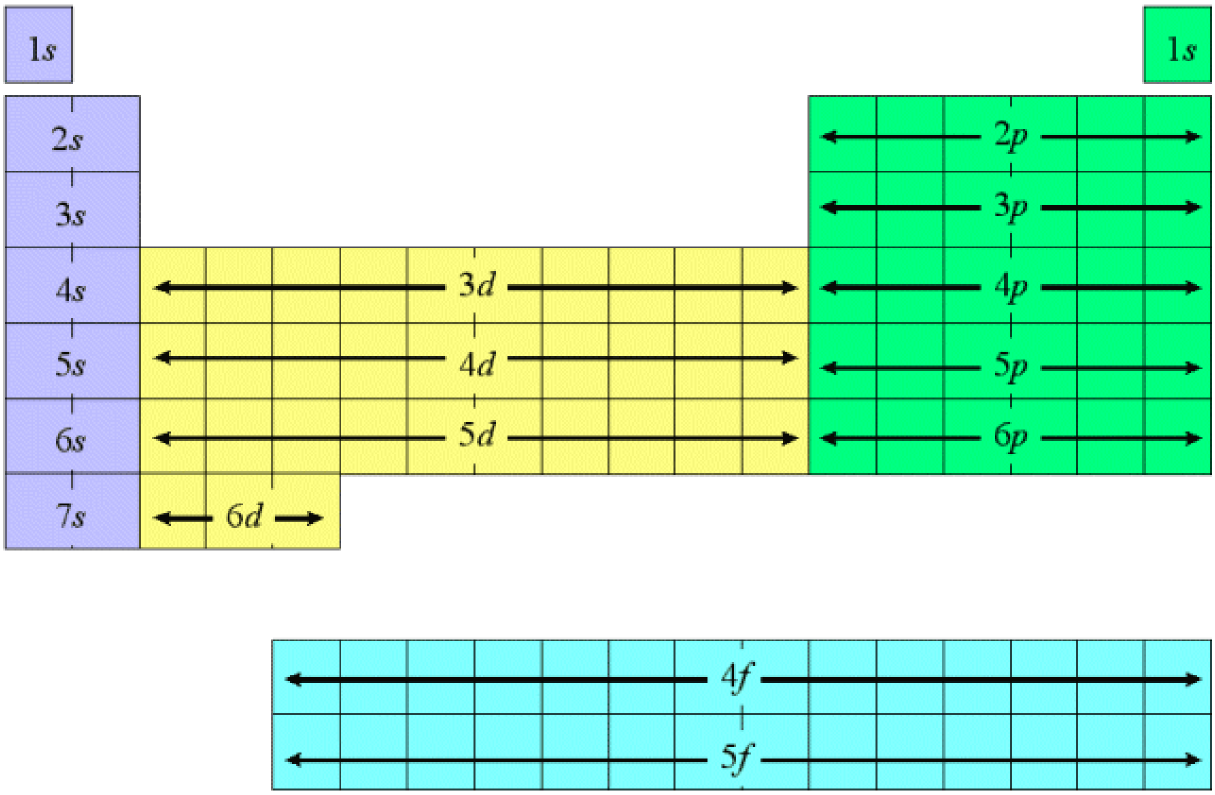
Electron Configuration

- *Pauli Exclusion Principle* - no two electrons in an atom can have the same four quantum numbers; no more than two electrons per orbital
- *Aufbau Principle* - electrons fill according to orbital energies (lowest to highest)

Electronic Structure of Atoms

Electron configurations and the periodic table

The periodic table is structured so that elements with the same type of valence electron configuration are arranged in columns.



- **The left-most columns include the alkali metals and the alkaline earth metals.** ***In these elements the valence <u>s orbitals</u> are being filled***
- **On the right hand side, the right-most block of six elements are those in which** ***the valence <u>p orbitals</u> are being filled***

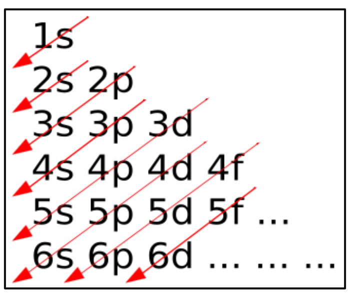
These two groups comprise the main-group elements

- **In the middle is a block of ten columns that contain** ***transition metals*****.** ***These are elements in which <u>d orbitals</u> are being filled***
- **Below this group are two rows with 14 columns. These are commonly referred to the** ***f-block metals*****. In these columns** ***the f orbitals are being filled***

Important facts to remember:

1. **2, 6, 10 and 14 are the number of electrons that can fill the *s, p, d* and *f* subshells (the *l*=0,1,2,3 azimuthal quantum number)**
2. **The 1*s* subshell is the first *s* subshell, the 2*p* is the first *p* subshell (n=2, *l*=1, 3*d* is the first *d* subshell, and the 4*f* is the first *f* subshell**

<u>The diagonal rule</u>



What is the electron configuration for the element Niobium? (41)

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^3$

Niobium is actually:

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ \underline{5s^1\ 4d^4}$

The reason is that the 5s and 4d energy levels are quite close and certain electronic arrangements can result in the levels being slightly different than expected.

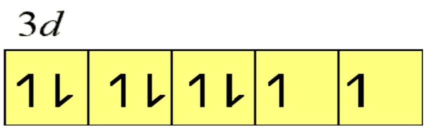
What is the electron configuration of the element Nickel? (28)

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$

What is the electron configuration for Nickel in terms of the nearest noble gas?

$[Ar]\ 4s^2\ 3d^8$

How would the last valence orbital be filled?



<u>Practice Electron Configuration and Orbital Notation</u>

Write the electron configuration and

orbital notation for each of the following

$Z = 20$

$Z = 35$

$Z = 26$

<u>Development of the Periodic Table</u>

The most significant tool for organizing and remembering chemical facts is the *periodic table*

- **Based on the periodic nature of electron configurations**
- **Elements in the same column have the same number of *valence electrons***
- **Similarities in chemical nature due to similarities in valence electron configuration**

Development of the Periodic Table

- **Certain elements, such as gold and silver, can be found *naturally* in their *elemental form* and were discovered thousands of years ago.**
- **Some radioactive elements are quite unstable and their isolation is dependent upon modern technology**
- **The majority of elements are stable, but commonly present in *compound* form with other elements**

In the 1800's methods were developed to isolate various elements from compound form

- **1800: 31 elements identified**
- **1865: 63 elements identified**

1869: Dmitri Mendeleev and Lothar Meyer published schemes for classifying elements

The elements could be ordered according to their atomic weight (i.e. grams/mole for the naturally occuring mixture of isotopic forms) which resulted in periodic characteristics

Mendeleev's insistence on ordering elements by atomic weight, and grouping them by characteristics resulted in several *"gaps"* in the table

- **Both Gallium (Ga) and Germanium (Ge) were unknown at the time**
- **Thus there was a gap under Aluminum (Al) and a gap under Silicon (Si)**
- **Mendeleev concluded therefore that there must be two elements, which he called "eka-Aluminum" and "eka-Silicon" which must fill these gaps**

Mendeleev predicted not only that Ga and Ge must exist, but also described some of their general physical properties

- **Their approximate atomic weight**
- **The stoichiometric relationship for compounds involving oxygen and chlorine**

Ga and Ge were discovered decades later, but their physical and chemical characteristics as predicted by Mendeleev were correct

The accuracy of Mendeleev's predictions for undiscovered elements, based on his periodic table, convinced scientists of its validity

1911 Rutherford model of the atom:

- **most of the mass of the atom was located in a dense nucleus**
- **the nucleus had a net positive charge**

- **beyond the nucleus was a mostly empty space which contained electrons with a net negative charge**

<u>1913 Henry Moseley (killed at Gallipoli at age 28)</u>

- **investigated the characteristic frequencies of X-rays produced by bombarding each of the elements in turn by high energy cathode rays (electrons).**
- **He discovered a mathematical relationship between the frequency and the atomic number (the "serial number" in the periodic table).**
- **This must mean that the atomic number is more than a serial number; that it has some physical basis.**
- **Moseley proposed that the atomic number was the *number of electrons* in the atom of the specific element.**
- **This also means that the atomic number is the number of positive charges carried by the nucleus.**

<u>Too Good to Be True?</u>

- **Not all elements follow the "order" of the diagonal rule**
- **Notable exceptions: Cu (Z = 29) and Cr (Z = 24)**

$$Cu = [Ar]4s^{1}3d^{10}$$

$$Cr = [Ar]4s^{1}3d^{5}$$

Reason: slightly greater stability associated with filled and half-filled *d* subshells

<u>Periodic Properties of the Elements</u>

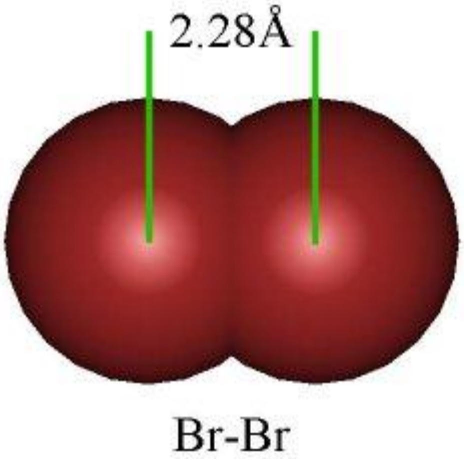
Three properties that provide important insights into chemical behavior include:

1. **atomic size**
2. **ionization energy**
3. **electron affinity**

<u>Sizes of atoms</u>

From the quantum mechanical model of atoms we can conclude that an atom does not have a sharply defined boundary. *This leads to a conceptual problem - just what exactly is the "size" of an atom?*

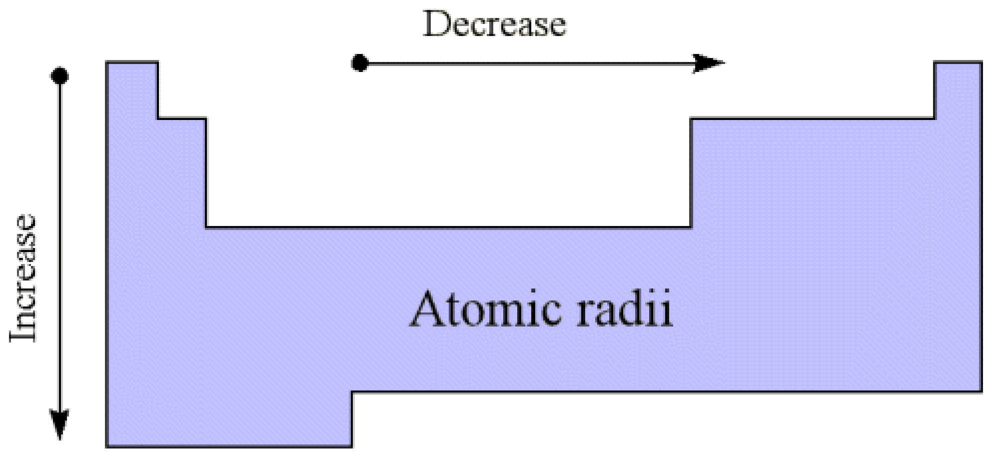
It is possible to estimate the atomic radius of an atom by assuming that atoms are spherical objects that touch each other when they are bonded together in molecules



- **The Br-Br distance in Br_2 is 2.28 Å, thus the radius of the Br atom is 1.14 Å**
- **The C-C bond distance is 1.54 Å, thus the radius of Carbon is 0.77 Å**

What are the general characteristics of atomic bond lengths as determined from bond-bond distances (small molecule crystallography, NMR, other methods)

- **Within the *columns* of the periodic table, the atomic *radii increase as you go down the column***
- **Within the *rows* of the periodic table, the atomic radii *decrease as you move to the right***



General trends for elements filling the *s* and *p* orbitals

What is the basis for these observations?

Two general factors affect the size of the outermost orbital:

- **The principle quantum number**
- **The effective nuclear charge**

Proceeding down a column:

- **The valence electrons are remaining constant**
- **The principle quantum number is increasing**
- **The shielding electrons are increasing, but so is the nuclear charge - the end result is that essentially the effective nuclear charge on the valence electrons is relatively constant**
- **Since the major effect is that the principle quantum number increases as you go down a column,** ***the atomic radius increases*** **.**
